

Raman spectroscopic analysis of a belltower commemorative wall decoration

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Abstract The Raman spectroscopic analysis of a rare wall decoration in a church belltower, depicting the initials of couples married there in circular roundels over some 230 years, since 1777, has been undertaken prior to their impending restoration. The spectral data indicate that the red pigment is exclusively haematite which has been applied to plaster which exhibits the signatures variously of calcite, gypsum, anhydrite, calcium phosphate and dolomitic limestone; evidence of amorphous carbon is attributed to the deposition of soot from candle illumination, which has been recorded in historical documentation. The presence of biosignatures attributed to carotenoids in several samples is evidence of biological colonisation and potential deterioration which requires special treatment in the restoration strategies. The blackened areas near the upper edges of the wall decoration indicate carbon deposition and organic contamination. The latest addition to the decoration accomplished in 2008 shows that haematite has been used over a calcite ground. In earlier dated specimens, the presence of limewash is evident, which has only been partially converted into calcite by aerial attack from carbon dioxide in moist conditions.

Keywords Wall paintings · Raman spectroscopy · Dated specimens · Calcareous ground · Biological deterioration

1 Introduction

The applicability of Raman spectroscopy to the analysis of archaeological artefacts and art works has been amply demonstrated in recent years [1–5]. From the identification of mineral pigment composition, degradation and substrates in ancient frescoes and wall paintings [6–10] and in polychrome statuary [11] to the discovery and evaluation of biological degradation in organic dyes [12, 13], textiles [14, 15], endangered rock art exposed to hostile environments [16–20] and on the pigments on historiated manuscripts and parchments [21–34] much novel information has been revealed at both a microscopic and macroscopic level of molecular interrogation. In particular, for manuscript pigment analysis and characterisation, a combination of Raman spectroscopic and other microanalytical techniques is found to be extremely useful. Several literature databases of characteristic Raman spectral signatures have been compiled, which assist the identification of pigments in these applications [35, 36]. An advantage of the application of the Raman spectroscopic technique to artefacts from depositional environments is that little or no chemical or mechanical preparation of specimens is required and the presence of water, which has a low Raman scattering cross-section, is not detrimental to the observation of spectral signals, unlike infrared spectroscopy where desiccation is often demanded in the preparation of samples for analysis. Hence, there are several examples of molecular information being provided from the Raman spectroscopic study of specimens from waterlogged burial sites [37, 38] and from wall paintings which are subject to the

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effects of moisture and efflorescence as frequently found in churches. Rock art and wall paintings in public places, such as caves and churches, is prevalent to deterioration caused as a result of human visitation and handling—this is found to be even more acute where the art works have been partially destroyed by heavy-handed restoration particularly in the 19th and early twentieth centuries and by deliberate acts of war and aggression: a recent example of this [39, 40] is provided by the restoration of a late Renaissance wall painting in a church in Valencia which has been severely damaged by automatic gunfire and conflagration during its occupation in the Spanish Civil War in the mid- to late-1930s. Raman spectroscopy has played a vital role in this particular case in the identification of the mineral pigments used originally, the location of areas of unsympathetic and incorrect restoration undertaken in the 1960s and in the early warning notice of regions of ongoing biological colonisation and degradation of the pigments near six unglazed lunettes in the church nave.

In the current study, we report the results of Raman spectroscopic analytical work undertaken upon a rather unusual wall decoration which has been added to over a period of some 230 years: the wall of the bellringers' loft in the bell tower of East Drayton church in Nottinghamshire in the UK has commemorative and dated circles (locally known as “cheeses” or “cake rings”) [41–45] which contain the initials of the bride and groom who have been married in the church (Figs. 1, 2). The earliest date recorded is 1777, up to 1865, after which in 1873 the ringers' loft was dismantled and ringing took place from the ground floor, with the painted area inaccessible until the ringers' loft was reinstalled in 1952. The latest “cheese” dates from 2008. The palette is apparently very simple and the decoration is applied in red over a creamy-white ground, covering the period from 1777 to 1865 with the latest “cheese” dated 2008, so overall



Fig. 2 “Cheese” decoration showing evidence of blackening and degradation

representing more than a period of 230 years. This decorative commemorative wall is now due for restoration and the opportunity has arisen for comprehensive sampling to be undertaken: during preliminary conservation studies it has become apparent that the wall painting is in need of extensive restoration and several parts are friable and have become detached from the substrate. An example of this is shown in the detail of the 1852 “cheese”. Also, a blackening of some parts of the wall painting can be seen in Figs. 2 and 3 and the reason for this is not immediately apparent. In this study, therefore, we need to address the following questions:

1. What is the composition of the red pigment used in the wall painting?
2. Has this pigment composition been changed with time over 230 years?
3. What is the nature of the substrate ground and can one identify any cause for its detachment?



Fig. 1 St Peter's Church, East Drayton, “cheese” wall decoration in the belltower



Fig. 3 Detail of the 1852 “cheese”

4. What is the origin of the blackening of parts of the wall painting? This blackening is restricted to the surrounding wall areas and does not occur inside the “cheeses”.
5. Is there any evidence spectroscopically of biological degradation which may have some influence upon the future integrity of the artwork?

2 Experimental

2.1 Specimens and sampling

The church of St. Peter in East Drayton in the Diocese of Southwell, Nottingham, United Kingdom, is of twelfth Century foundation [46]: this is known because Geoffrey Fitz Peter, Earl of Essex, renounced all his rights in the chapel of Drayton in favour of the canons of the chapter of York between 1199 and 1213, and a late C12 chamfered, arched doorway exists in the chancel. It remained appropriated to York during the medieval period: the fifteenth century bell tower contains a commemorative decoration relating to the marriage ceremonies of the bell ringers, consisting of dated circles known locally as “cheeses” or “cake rings” with initials from 1777 to 1865 with a single entry in 2008 (there was a gap from 1873 to 1952 when there was no ringers’ gallery and the painted wall was inaccessible). In this study, during a preliminary restoration assessment, specimens of the decoration were taken from “cheeses” by scalpel excision ranging from 1788 to 2008, comprising the years: 1786, 1799, 1800, 1803, 1818, 1835, 1852, 1853 and 2008 with a further five specimens taken specifically from the blackened areas and edging. The uppermost paintings are not now easily accessible as the original ringers’ gallery was higher than the present floor.

The nearby medieval church of St. Peter, Laneham, 4 km to the north-east, also has a set of similar “cheeses” in the ringing chamber of the tower, although far fewer than at East Drayton and within a much more restricted date range, with visible dates running from 1816 to 1837. Some of these “cheeses” are shown in Fig. 4.

2.2 Raman spectroscopic analysis

Raman spectra were obtained using a range of excitation wavelengths: 532 nm from an argon ion gas laser, and 785 and 1064 nm excitation from diode lasers. A Raman microscope was used to obtain spectra from several areas of interest in each sample. Fourier transform Raman spectra were recorded using a Bruker RFS 100 instrument with Nd³⁺: YAG laser and the nominal maximum laser power was 160 mW to prevent sample damage; 1000 spectral scans at a spectral resolution of 4 cm⁻¹ were accumulated. A SENTERRA dispersive Raman microscope instrument



Fig. 4 St Peter’s Church, Laneham, “cheese” decoration in belltower

operating at 532 and 785 nm equipped with cooled charge-coupled detector with the incident laser beam focused on the sample with a 50× objective was also used. Good spectra were obtained using a range of laser powers of 0.2–2.0 mW and 10 accumulations for 10 s at a spectral resolution of 3–5 cm⁻¹.

2.3 Results and discussion

The results from an analysis of the Raman spectra are summarised in Table 1 and a selection of the spectra of pigments and grounds (referred to as “white side”) are shown in Figs. 5A, B, 6A, B and 7; the following features of interest are highlighted:

1. The red pigment used is exclusively haematite, iron (III) oxide [47]: the sharpness of the bands seem to indicate that it is quite crystalline and not adulterated with clays as in the generic “red ochres”. The usage of this pigment has not changed with decoration over the period of 220 years and haematite has been used throughout from 1786 to 2008.
2. The nature of the ground deserves some comment: in 1786, signals from gypsum were detected along with those from calcite. In 1799, 1800 and 1803, only gypsum was detected, whereas in 1818 gypsum and calcite were detected together. Then, in 1852 clear signals assignable to a dolomitic limestone were found and in 1853 weak signals possibly of magnesite were detected, and finally in 2008, the last “cheese” sampled, only signals of calcite were detected [48].
3. The nature of the blackening of the wall decoration is revealed by the Raman spectra from 1803 to 1852, where clear signals of carbon are noted (represented by the so-called D and G bands of sp² and sp³ hybridised carbon at 1320 and 1580 cm⁻¹). This carbon is not graphitic and therefore is more likely to be soot [49, 50].
4. The analyses of the extensively blackened and green-stained areas, seen in Figs. 2 and 3, show rather more

Table 1 East Drayton Church: Bellringers' "Cheese" samples Raman spectroscopic analysis

1786	Pigment minor calcite (1085), anhydrite II/bassanite (1015), haematite (223, 290, 406) Substrate gypsum (1007), minor calcite (1085,280), (1028) anhydrite III
1799	Pigment biodegraded (1525, 1157, 1002), carotenoid, plus other organic signals (1457, 1444, 1349, 1205, 1184, 965) Substrate gypsum
1800	Pigment gypsum, haematite Substrate gypsum
1803	Pigment carbon (1320, 1580), gypsum, haematite, anhydrite III (1024) Substrate gypsum
1818	Pigment gypsum, carbon, calcite, haematite, anhydrite III (1026) Calcite, minor gypsum, minor lead white (1050) Substrate calcite, limewash putty
1835	Pigment gypsum, haematite, anhydrite III (1025) Substrate gypsum
1852	Pigment gypsum, carbon, haematite, anhydrite III (1025) Substrate gypsum, dolomite (1097, 724, 299)
1853	Pigment carbon, haematite, gypsum, magnesite (1111) Substrate calcite
2008	Pigment calcite, haematite Substrate calcite, carbon
Border Black North Wall Lower	Gypsum, carbon
Border Trefoil Lower	Gypsum, carbon, minor calcite
BYN 0001a White	Gypsum, calcite, organics
BYN 0001b	Phosphate (1073, 963, 588, 433), organics (1073, 1050,1245)
BYN 0001b green stains	Cyanobacterial (1600, 1275, 1196, 812, 761, 507 480), gypsum

Numbers in brackets are spectral wavenumbers/cm⁻¹

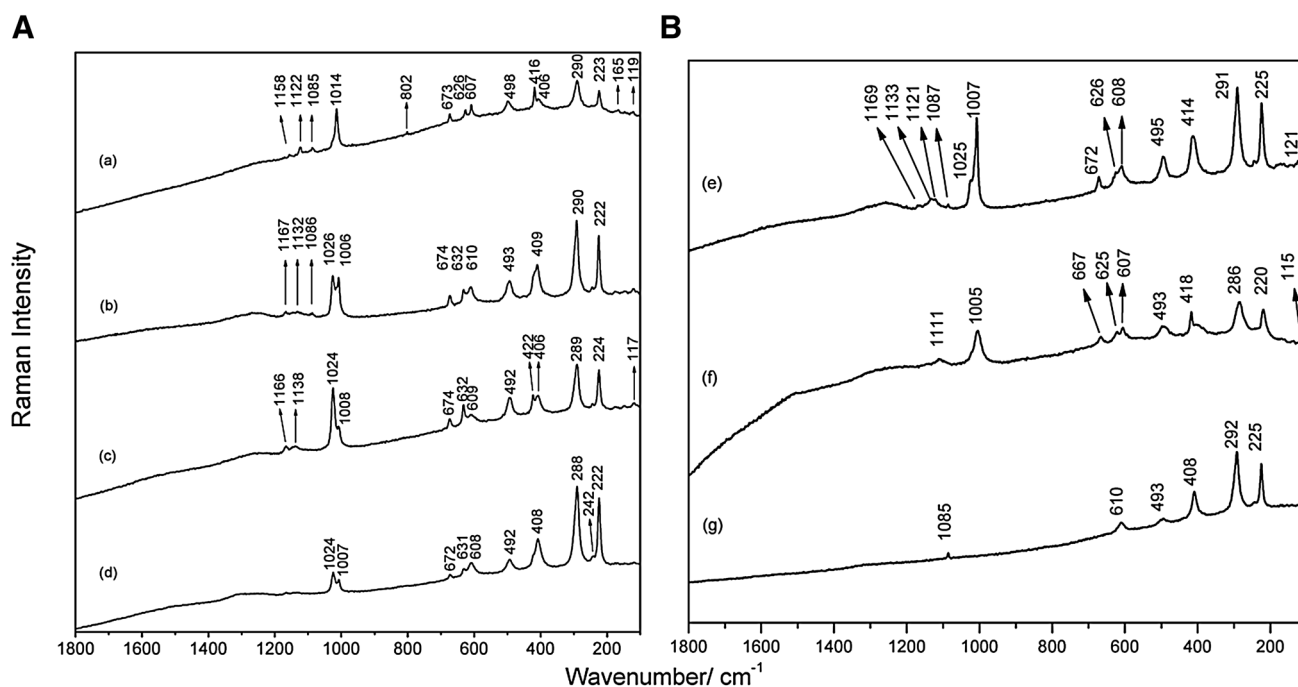


Fig. 5 **A, B** Stackplotted Raman spectra of pigment samples from "cheese" specimens from 1786 to 2008, and of the three BYN specimens: BYN 001a, BYN 001b and BYN 001 green stains. Laser excitation 785 nm in all cases; wavenumber range 100–1800 cm⁻¹

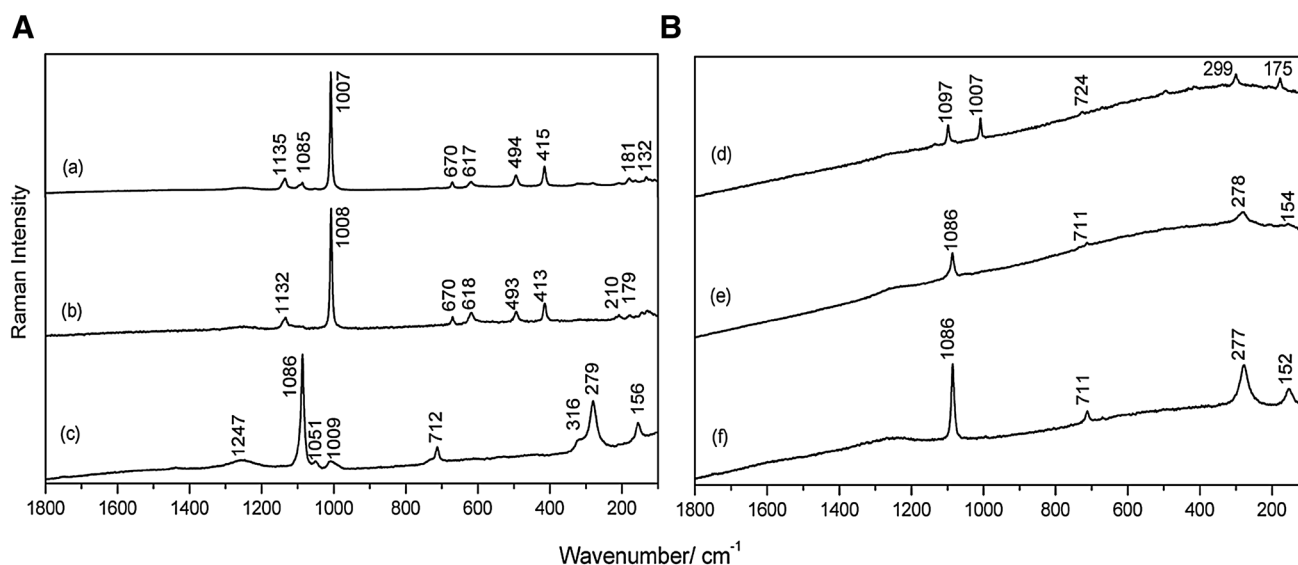


Fig. 6 A, B Stackplotted Raman spectra of ground samples from “cheese” specimens from 1786 to 2008. Laser excitation 785 nm in all cases; wavenumber range 100–1800 cm^{-1}

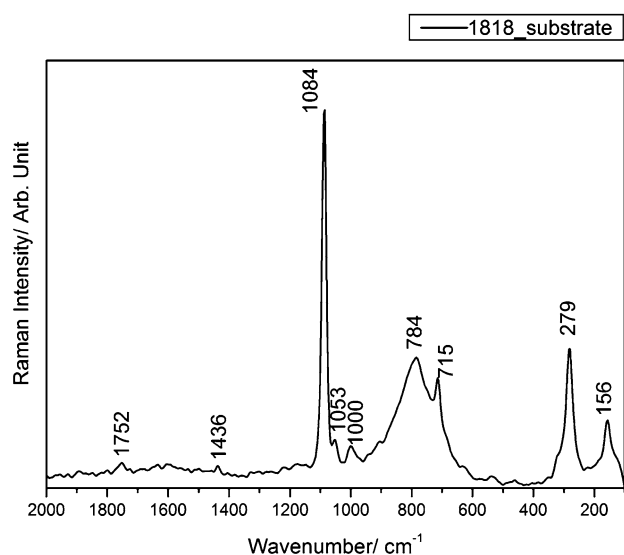


Fig. 7 FT Raman spectrum of the 1818 “cheese” substrate, 1064 nm excitation, wave number range 100–2000 cm^{-1} , showing evidence for the use of limewash putty with the broad signal at 784 cm^{-1} , which has only been partially converted into calcite

complex spectra with features recognisable from carotenoids, chlorophyll and other organic compounds, which indicates that biodeterioration has occurred in these areas [51–53]. This is also noteworthy in the “cheese” from 1799. The carotenoid is probably beta-carotene and reflects cyanobacterial or lichen colonisation of the affected areas and this is particularly prevalent in the border-blackened areas.

5. The presence of calcium phosphate with its characteristic sharp signal at 963 cm^{-1} is noteworthy in the BYN0001 a and b specimen regions (Fig. 5)—the only location identified for this material in the current study. Calcium phosphate is the major component of calcined bone ash [54, 55] and its presence here can only be a matter of conjecture—clearly it has no relevance to the decorative pigment and its detection in wall paintings usually implies that bone black or ivory black has been used as a carbon-based pigment by the artist [2, 3]. However, there is no indication of carbon otherwise having been deliberately added to this area of the painting.

There are several important conclusions to be drawn from these spectral data: the change in composition of the white ground needs to be explained. From the earliest to the last decorative “cheese” sampled in the current study, the presence of calcite is noted: additional Raman spectra carried out with 1064 nm excitation and a Fourier Transform Raman Spectrometer clearly show the presence of limewash putty [56] remains in only the 1818 sample (Fig. 7)—this was a method of substrate preparation devised by Roman artists and is well described in the available literature. It consisted of the calcination of calcium carbonate, calcite, dolomite or aragonite, to form lime which was then partially slaked with water into a sticky moist composition and then applied as a rendering to walls and often used as a mortar from medieval period onwards. In moist conditions, exposure to atmospheric carbon dioxide then re-converted the limewash putty into a hard calcite. Here, we see evidence that this conversion has not gone to completion in

the 1818 “cheese” sample and the broad feature centred at 784 cm^{-1} assignable to an electronic excitation of calcium oxide/hydroxide confirms this, with the additional features of calcite at 1084 , 712 and 273 cm^{-1} . There are a variety of reasons to explain this observation, one of which is that the formation of an initial skin of hard, non-porous calcite has protected the underlying lime substrate from an ingress of carbon dioxide and water [37]. It is interesting that the Raman spectral signal of incomplete conversion of lime into calcite has not been found in the ground materials elsewhere: this does not mean that limewash putty usage is unique to the 1818 cheese ground preparation but rather that residual unconverted lime has been preserved here locally.

In addition, the presence of gypsum is revealed throughout the sampling of the pigment and ground, except for the latest 2008 “cheese” sample ground which is indicative of calcite alone. There are two possible explanations for this observation: first, the original decorators used a Romanesque mixture of gypsum and calcite in their substrate, which was often seen as occurring in the transition period from medieval to Renaissance wall paintings [57] and is therefore rather out of period to be postulated here. Second, the reaction of sulphur dioxide from burning candles and incense resins with calcite produces gypsum, in a sulfonation of the carbonaceous support. The result of this process is the removal of calcium carbonate and its substitution with its friable sulphate analogue—which could explain the surface deterioration and detachment of areas of the painting noted by the restorers. The 2008 “cheese” does not exhibit such a signal and this could be ascribed to the cleaner air in the bell tower presumably by the replacement of candles and oil lamps with electric lighting? That candles were burned during ringing is certain as we have a reference from the church account book in 1773 to the expenditure of 3d for ‘ $\frac{1}{2}$ pound candles for the ringers’. A further analytical conclusion regarding the composition of the ground can be made with the observation of the Raman signatures of other species in the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – CaSO_4 system where bands at 1015 and 1024 – 1026 cm^{-1} have been recorded: reference to the comprehensive analytical studies of Prieto-Taboada et al. [58, 59] which have been reported on this system reveals that we see the presence of dehydrated forms of gypsum, namely anhydrite II /bassanite and anhydrite III—where anhydrite II and II are both completely dehydrated CaSO_4 and bassanite is the hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. These dehydrated forms of gypsum are seen in the “cheeses” from 1786, 1803, 1818, 1835 and 1852 and probably reflect the results of changing environmental moisture conditions operating in the belltower ringing chamber which may partially account for the observed instability of the substrate and its detachment from the walls.

A point of interest in the ground or substrate composition relates to the 1852 and 1853 samples where Raman signals of dolomite and calcite, respectively, are observed. This is suggestive of the use of calcite and a magnesium-rich calcite or dolomitic limestone as ground material over this narrow period of time reflecting a different possible source of this material.

Finally, comment must be made about what is undoubtedly the most obvious disfigurement of this wall painting, namely, the observed and unsightly blackening, which is particularly extreme in the regions surrounding the earlier “cheeses” and their edges. Amorphous carbon has been detected in the spectra of several specimens and its origin could arise from two possible sources: first, the deliberate addition of carbon black or soot to the red haematite pigment to darken its colour; however, the reason for this would be obscure since it does not occur everywhere. Second, it is well known that ancient wall paintings in churches and places of worship do suffer from the deposition of soot from candles and oil lamps and these deposits are often irregular and are dependent upon the proximity of the lighting source, draughts and type of illumination used. The heaviest soot deposits here seem to be located in the higher regions of the painting and at the upper edges as would be expected in this case; it is also interesting to note, however, that these same areas give spectral signatures indicative of biodeterioration namely organic biomarker molecules characteristic of biological colonisation. In particular, the presence of carotenoids and chlorophyll are noted from the spectral data, indicative of bacterial and lichen communities. Cyanobacterial colonisation would demonstrate the presence of their unique biomarker, scytonemin [60, 61], which is not recognised here. The use of Raman spectroscopy to identify the presence of biological degradation of artworks, especially those which have been exposed to environmental stresses, is now well appreciated and this study provides another example of this application: it is of crucial importance for the conservation of a wall painting that the presence of potentially ongoing biodegradation is recognised in the restorative and protective strategy as failure to deal with this appropriately will result in even more severe and irreversible damage being caused if left untreated. The case of the 16th Century Renaissance wall paintings by Zuccari in an open courtyard in the Palazzo Farnese in Caprarola north of Rome is documented [62–64], where Raman spectroscopy identified the presence of *Dirina massiliensis* forma *sorediata* lichen colonies which over the course of many years had invaded the frescoes and had destroyed some 80% of the visible artwork and through the conversion of the underlying calcite into hydrated calcium oxalate, whewellite and weddellite, had resulted in the irreversible detachment of large areas of the artwork from the wall. Clearly therefore, evidence

of biodeterioration of an artwork being subject to preservation, whilst unpleasant news for restorers and conservationists is the prime candidate for urgent appraisal and treatment, so its presence here is an important discovery from the spectral data.

A final comment should be made about preliminary analyses which were similarly carried out on three Laneham church “cheeses” dating from 1816, 1825 and 1830 (Fig. 4), where the pigment in the 1816 cheese shows the presence of goethite, whereas that in the two others is strictly haematite; the substrates are calcite for the first two samples and bassanite for the 1830 sample—which is the only one to also show the presence of soot. The presence of goethite in the earliest example could indicate that a mixture of goethite and haematite was used here or that goethite was heated to produce the desired colour—upon heating to 300 °C goethite transforms into haematite, with a consequent variation in colour occurring from yellow to orange-red—with such a procedure residual goethite often can be detected in the haematite pigment used.

3 Conclusions

The conclusions arising from this analytical study can be summarised as follows:

1. The coloured pigment has not changed in composition over the time span of the sampling regime, some 230 years, comprising haematite in a well-crystallised form.
2. The ground materials used show significant differences and encompass calcite, aragonite, dolomite and bassanite.
3. The blackened areas evident in the upper reaches of the wall painting give some spectral signatures associated with biological colonisation: this can be extremely unsightly and deleterious, and if not arrested, it provides an ongoing source of potential detachment of the painted areas from the wall through hyphal penetration of the substrate plaster and ground.

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